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U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

REMARKS

This Amendment amends claims 30-33. Claims 16, 18, 19 and 24-34 are pending.

Examiner Fubara is thanked for withdrawing the indefiniteness rejection of claims 34, 16, 18 and 19. However, the undersigned is unsure exactly what is meant by paragraph 6 of the Official Action. Method claim 34 includes a correlation step in which the desired biodegradability of a silica fiber is correlated with the viscosity of a silica sol. Spinning is begun when the silica sol's viscosity reaches a value correlating to the desired biodegradability of the silica fiber. While silica solubility in SBF is a quantitative measure of a silica fiber's biodegradability, claim 34 does not require measurement of silica solubility in SBF.

This Amendment overcomes the 35 U.S.C. § 112, second paragraph, rejection of claims 24-30. "Controllably" has been deleted from claims 30-33. Reconsideration and withdrawal of the indefiniteness rejection of claims 24-30 are earnestly requested.

This Amendment also overcomes the 35 U.S.C. § 112, first paragraph, rejection of claims 24-30. "Controllably" has been deleted from claims 30-33. Reconsideration and withdrawal of the

6

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

§ 112, first paragraph, rejection of claims 24-30 are earnestly

requested.

The 35 U.S.C. § 112, first paragraph, rejection of claims 34,

16, 18 and 19 for failure to comply with the written description

requirement is traversed.

At the outset, the written description requirement is separate

and distinct from the enablement requirement of 35 U.S.C. § 112,

first paragraph, <u>Vas-Cath, Inc. v. Mahurkar</u>, 935 F. 1555, 1560, 19

USPQ2d 111, 1114 (Fed. Cir. 1991)[1]. An applicant shows possession

of the claimed invention by describing the claimed invention with

all of its limitations using such descriptive means as words,

structures, figures, diagrams and formulas that fully set forth the

claimed invention, <u>Lockwood v. American Airlines, Inc.</u>, 107 F.3d

1565, 1572, 41 USPQ2d 1961, 1966 (Fed. Cir. 1997). The fundamental

factual inquiry is whether the specification conveys with

reasonable clarity to those skilled in the art that, as of the

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[1]The Official Action appears to confuse the written
description requirement with the enablement requirement, using
phrases such as "invitation to experiment", "invited to try" and
"unduly experimenting". These arguments go to whether the
applicants have provided an enabling description such that one of
ordinary skill in the art would not have to perform undue
experimentation to practice the claimed method. It is respectfully
submitted such enablement arguments have no place in a written
description rejection, <u>Vas-Cath</u>, <u>supra</u>.

7

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

filing date of the application, the applicants were in possession

of the invention as now claimed, <u>Vas-Cath</u>, <u>supra</u>, at 1563-64, 19

USPQ2d at 1117.

In this case, the answer to this "fundamental inquiry" is <u>yes</u>

- the application as filed <u>does</u> convey, with reasonable clarity to

those skilled in the art, that the applicants were in possession of

the presently-claimed invention as of the application's filing

date.   Independent claim 34[2] recites a method for preparing a

biodegradable silica fibre, comprising

correlating a desired biodegradability of a silica fibre with

a viscosity of a silica sol,

preparing a silica sol, and

spinning a fibre from said silica sol,

wherein the spinning process is begun when the viscosity of

the silica sol reaches a value correlating to said desired

biodegradability of the silica fiber.

The specification does <u>not</u> use the same words as the

correlation step of claim 34 ("correlating a desired

biodegradability of a silica fibre with a viscosity of a silica

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[2]   Claims 16, 18 and 19 depend directly or indirectly from
claim 34.

8

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

sol"). However, the written description requirement does <u>not</u>

require explicit recitation of the precise words of claim 34:

> A claim will not be invalidated on section 112
> grounds simply because the embodiments of the
> specification do not contain examples explicitly covering
> the full scope of the claim language. See <u>Union Oil Co.</u>
> <u>v. Atlantic Richfield Co.</u>, 208 F.3d 989, 997 (Fed. Cir.
> 2000). That is because the patent specification is
> written for a person of ordinary skill in the art, and
> that person comes to the patent with the knowledge of
> what has come before. <u>In re GPAC Inc.</u>, 57 F.3d 1573,
> 1579 (Fed. Cir. 1995). Placed in that context, it is
> unnecessary to spell out every detail of the invention in
> the specification; only enough must be included to
> convince a person of ordinary skill in the art that the
> inventor possessed the invention and to enable such
> person to make and use the invention without undue
> experimentation.

<u>Lizardtech, Inc. v. Earth Resource Mapping, Inc.</u>, 424 F. 3d 1336,

1345, 76 USPQ2d 1724 (Fed. Cir. 2005), <u>rehearing en banc denied</u>,

433 F.3d 1373, 77 USPQ2d 1391 (Fed. Cir. 2006). In this case, one

of ordinary skill in the art would understand the applicants

possessed the correlation step of claim 34 when they filed this

application in view of the following disclosures:

1.   "The method for preparing a controllably biodegradable

     silica fibre of the present invention comprises spinning

     the fibre from a silica sol, wherein the starting point

     of the spinning process is controlled by the viscosity of

     the silica sol." (Page 5, lines 25-28).

9

2.   "The controllably biodegradable silica fibre of the

present invention is spun from a silica sol, the

biodegradation of the fiber being controlled

by...controlling the starting point of the spinning

process by the viscosity of the silica sol." (Page 6,

lines 5-8).

3.   "The silica sol is spinnable within a certain time period

rather than at a single point and the viscosity of the

silica sol increases during that time period...The fibers

spun in the early stage of the spinnability period

degrade more slowly...than the fibres spun in the later

stage of spinnability." (Specification, page 5, lines

12-20).

4.   "The fibres derived from the sols which have low

viscosity during the spinning process degrade slower than

fibres derived from sols prepared at higher spinning

viscosity. Accordingly, the starting point of the

spinning process is important regarding the

biodegradation. The fibres spun...in the early stage of

spinnability degraded very slowly as compared to fibres

10

spun in the later stage." (Specification, page 16, lines 17-21).

5. <u>Fig. 5</u> - Figure 5 shows the viscosity of three silica sols as a function (<u>i.e.</u>, correlation) of the starting point of the spinning process for silica fibres (Specification, page 4, lines 3-4). The fiber spinning time period is shown as beginning when the viscosity of the silica sols reaches a value of 2 Pas. The viscosity of each silica sol increases over time. Eleven different fibres were prepared at different time/viscosity starting points.

The application thus teaches that if you wish a more biodegradable fiber you should begin spinning in the later stage of the spinning period. Conversely, if you wish a fiber to degrade more slowly you should begin spinning at an earlier stage of the spinning period. One of ordinary skill in the art would understand the applicants possessed the step of "correlating" a desired biodegradability of a silica fibre with a viscosity of a silica sol.

The Official Action appears to base its written description rejection on non-enablement grounds. As discussed above, such

11

arguments are not relevant to a written description rejection.

Moreover, the specification <u>does</u> provide clear guidance as to when

to begin fiber spinning. Thus, page 5, lines 27-30 provide an

upper limit and preferred ranges for the viscosity of the silica

sol ("The viscosity of the silica sol at the starting point of the

spinning process is below 100 000 mPas". Preferably it varies in

the range of 1000 - 50000 mPas, and more preferably in the range of

2000-15 000 mPas"). Original claims 2-4, among others, recite

these ranges and the viscosity maximum of below 100 000 mPas.

Example 3 and Fig. 5 provide additional guidance, for three

specific silica sols, as to when to initiate[3] the fiber spinning

process. According to Fig. 5, spinning ought to begin during the

time period when the sol viscosity is 2 Pas or above. Figs. 9 and

10 confirm fiber spinning can begin until the viscosity of the

spinning sol reaches 100 Pas.

One of ordinary skill in the art could easily follow the

procedures set forth in Example 1 to produce a series of silica

fibers at different times in the spinnability period, measure the

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[3]As shown in Fig. 5 the viscosity of a silica sol increases
with time. One of ordinary skill in the art would know there is
always a (lower) starting sol viscosity and a (higher) ending sol
viscosity when a fiber is spun from the silica sol.

12

biodegradability of the fibers actually produced using the procedures described in Example 3, and construct a graph similar to Fig. 5 (or a table similar to Table 3) correlating, for each fibre produced, the viscosity of the silica sol when fiber spinning began with the fiber's biodegradability, assuming other factors are held constant.[4] These procedures are <u>routine</u> experimentation to one of ordinary skill in the art.

In short, one of ordinary skill in the art would understand that, at the time their application was filed, the applicants had possession of the correlation between a fiber's biodegradability and the viscosity of the spinning sol at the point fiber spinning is begun. In addition, the specification provides one of ordinary skill in the art with more than sufficient guidance to be able to practice the claimed method without the exercise of <u>undue</u> experimentation. Reconsideration and withdrawal of the § 112, first paragraph, rejection of claims 34, 16, 18 and 19 are earnestly requested.

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[4]One of ordinary skill in the art would know a specific fiber's biodegradability will be dependent on additional parameters such as, for example, silica sol composition, fiber spinning conditions and aging conditions.

13

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

The 35 U.S.C. § 103(a) rejection of claims 16, 18, 19 and 34 over PCT Patent Publication WO 97/45367 to <u>Ahola et al.</u> is respectfully traversed.   Method claim 34 includes a correlation step in which the desired biodegradability of a silica fiber is correlated with the viscosity of a silica sol.   Spinning is begun when the silica sol's viscosity reaches a value correlating to the desired biodegradability of the silica fiber.

<u>Ahola et al.</u> fails to raise a <u>prima facie</u> case of obviousness against the claimed method because this reference fails to disclose or suggest the correlation step of claim 34.   <u>Ahola et al.</u> does not disclose or suggest the initiation of a spinning step at a specific viscosity <u>to produce a silica fiber having a desired degree of biodegradability</u>.

The Patent Office appears to argue that <u>Ahola et al.</u> must have mentally made the correlation required by claim 34.   First, there is no disclosure in <u>Ahola et al.</u> of such a mental correlation. Instead, the Patent Office is engaging in hindsight interpretation of the reference, aided by the applicants's specification.   Second, <u>Ahola et al.</u> discloses many parameters which are claimed to have a major or minor influence on fiber biodegradability, including diameter of the single gel-object and its production method,

14

sintering temperature, TEOS:H_2O molar ratio, pH of the silica sol,
aging, gelation rate, gel thickness, and drying. See page 8, line
7 to page 9, line 4. One of ordinary skill in the art is simply
given no disclosure or suggestion to correlate fiber
biodegradability with the viscosity of its silica sol at the point
when fiber spinning was begun.

The Patent Office mischaracterizes the correlation step of
claim 34 as an "arbitrary determination of when the spinning of the
fiber would begin". The plain words of the claim make clear that
the determination of when to start the fiber spinning process is
based on the production of a fiber having a desired
biodegradability, and thus is not arbitrary. One cannot
arbitrarily choose to start fiber spinning at any viscosity and
obtain a silica fiber having the desired biodegradability.

The Examiner's argument that Ahola et al.'s decision to begin
spinning at 10 mPas[5] suggests they correlated spinning viscosity

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[5]The 10 mPas viscosity value is believed to be erroneous
because fibers can be drawn from a silica sol only if the viscosity
is greater than or equal to 1000 mPas. See Sakka et al., "The Sol-
Gel Transition in the Hydrolysis of Metal Alkoxides in Relation to
the Formation of Glass Fibers and Films," 48 J. Non-Crystalline
Solids 31-46 (1982) at page 43, third paragraph of point 4.3.
Please note that 10P (Poise) is equal to 1000 mPas because 1
centipoise is equal to 1 milliPascal second.

15

with desired fiber biodegradability is completely unsupported by the reference.   Instead, <u>Ahola et al</u>. expressly teaches the diameter of the single gel object and the production method have a "profound influence" on the xerogel's dissolution rate.   The production methods involved production of particles by traditional crushing and by spray drying (Page 8, line 29 to page 9, line 4).

Reconsideration and withdrawal of the obviousness rejection of claims 16, 18, 19 and 34 over <u>Ahola et al</u>. are earnestly requested.

The 35 U.S.C. § 103(a) rejection of claims 34, 16, 18 and 19 over U.S. Patent No. 4,919,871 to <u>Lin et al</u>. is traversed. Method claim 34 includes a correlation step in which the desired biodegradability of a silica fiber is correlated with the viscosity of a silica sol. Spinning is begun when the silica sol's viscosity reaches a value correlating to the desired biodegradability of the silica fiber.

<u>Lin et al</u>. fails to raise a <u>prima facie</u> case of obviousness against the claimed method because this reference fails to disclose or suggest the correlation step expressly required by claim 34. Instead, the reference merely teaches permitting hydrolysis and condensation reactions to proceed until the sol has a suitable viscosity for fiber forming (Col. 2, line 67 to Col. 3, line 1).

16

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

Ageing of the sol to "a desired spinning viscosity" does <u>not</u>

disclose or suggest correlating the production of a silica fiber

having a desired degree of biodegradability with the initiation of

fiber spinning at a particular sol viscosity.

Lin et al. does <u>not</u> disclose or suggest that its fibers are

biodegradable.[6] The Patent Office argument that "biodegradability

is relative" is an improper attempt to read "biodegradable" out of

the claim, and cannot substitute for a <u>disclosure</u> (by column and

line number) or other factual <u>evidence</u> that the <u>Lin et al.</u> fiber is

biodegradable.

Similarly, the Patent Office cannot eliminate the claimed

correlation step by terming it "arbitrary" - the plain words of the

claim make clear that the determination of when to start the fiber

spinning process is based on the production of a fiber having a

desired biodegradability, and thus is <u>not</u> arbitrary. One cannot

"arbitrarily" choose to start fiber spinning at any viscosity and

obtain the desired biodegradability.

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[6] A biodegradable silica fiber has numerous hydroxyl groups on
the fiber surface. <u>See</u> <u>German '551</u> at page 4, line 21 to page 5,
line 4. In contrast, <u>Lin et al.</u> teaches drying its silica fibers
in an ammonia atmosphere, which will condense the hydroxyl groups
to hydrophobic siloxane groups (Si-O-Si-) and at the same time the
fiber's porosity will be reduced. The basis of the silica fiber's
biodegradability is effectively destroyed.

17

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

Lin et al. is directed to an entirely different problem (fiber stickiness). One of ordinary skill in the art, having read Lin et al., would have no basis to believe that (1) its fibers are biodegradable, or (2) that the biodegradability of its fibers could be varied by beginning the fiber spinning process at different times during the spinning time period.

Reconsideration and withdrawal of the obviousness rejection of claims 34, 16, 18 and 19 over Lin et al. are earnestly requested.

The 35 U.S.C. § 103(a) rejection of claims 24-33 over Ahola et al. is also traversed. A feature of claims 24-33 is a biodegradable silica fiber having a solubility in simulated body fluid of from 0.2 to 20 wt-%/h. The slowest (0.2 wt-%/hour minimum) solubility rate means that the fiber will completely dissolve in about 21 days.

Ahola et al. fails to raise a prima facie case of obviousness against the claims because this reference fails to disclose or suggest the 0.2 to 20 wt-%/hour silica solubility range feature of the claimed biodegradable fiber. Instead, most of the fibers of Example 2 of Ahola et al. did not dissolve at all in vitro, and there was no dissolution at all after two weeks in vivo.

18

The Example 2 fibers were either put into aqueous solution within 48 hours or 4 months later. Some of the fibers were treated at 300°C or 700°C as opposed to room temperature. As expressly stated in Example 2:

> Only the fibers kept at room temperature dissolved at any significant amounts. The RT-fibers stored for 4 months in an excicator dissolved 10 w-% within 4 weeks. (Page 14, lines 18-20; emphasis added).

Thus, most of the fibers of Ahola et al.'s Example 2 did not dissolve in vitro. The only fiber with appreciable dissolution had a solubility rate of 10 wt-%/4 weeks, or 0.0148 wt-%/hour, which is approximately 20 times slower to dissolve than the claimed biodegradable fiber. The Ahola et al. fibers will require 40 weeks to dissolve completely.

This is supported by the in vivo data of Example 2. Both sintered and non-sintered silica-xerogel fibers of Example 2 were surgically implanted into rats and then examined after two weeks. There was no sign of fiber resorption under scanning electron microscope.[7]

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[7]Ahola et al.'s statement that the fibers had been integrated into the surrounding connective tissues after two weeks of implantation does not mean the fibers dissolved. See the next sentence ("No signs of resorption of the fibers could be observed by SEM examination"). Instead, fiber "integration" simply means the fibers mixed with the surrounding connective tissue.

19

It is respectfully submitted the fast dissolution times of the claimed fiber are surprising and unexpected because the prior art simply had not achieved such fast dissolution times. The non-dissolving and slowly-dissolving fibers of <u>Ahola et al</u>. support this position.

Reconsideration and withdrawal of the obviousness rejection of claims 24-33 over <u>Ahola et al</u>. are earnestly requested.

The 35 U.S.C. § 103(a) rejection of claims 16, 18, 19 and 24-34 over German patent DE 196 09 551 ("<u>German '551</u>") is respectfully traversed. The patentable features of method claims 34, 16, 18 and 19 are discussed separately from the patentable features of the fiber/delivery device/pharmaceutical composition and method of treatment claims 24-33.

1.   <u>Method Claims 34, 16, 18 and 19</u>

Method claim 34 includes a correlation step in which the desired biodegradability of a silica fiber is correlated with the viscosity of a silica sol. Spinning is begun when the silica sol's viscosity reaches a value correlating to the desired biodegradability of the silica fiber.

<u>German '551</u> fails to raise a <u>prima facie</u> case of obviousness against the claimed method because this reference does not

20

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

disclose, teach or suggest the correlation step of the claimed

method.   Merely deciding to initiate spinning of the sol at a

specific viscosity does <u>not</u> perform, disclose, teach or suggest a

correlation step between desired biodegradability of the silica

fiber and a specific sol viscosity.

German '551 teaches that silica fiber biodegradability can be

controlled through silanol content (English translation, page 5,

lines 21-26). However, one of ordinary skill in the art is given

no suggestion or motivation to select a particular viscosity at

which to begin spinning the fiber to achieve a desired fiber

biodegradation rate.

A decision when to start spinning does not disclose or suggest

a correlation between the biodegradability of a silica fiber and

the viscosity of a silica sol at the point in time fiber spinning

is begun.   Nor can the Patent Office eliminate the claimed

correlation step by terming it "arbitrary" – the plain words of the

claim make clear that the determination of when to start the fiber

spinning process is based on the production of a fiber having a

desired biodegradability, and thus is <u>not</u> arbitrary. One cannot

"arbitrarily" choose to start fiber spinning at any viscosity and

obtain the desired biodegradability.

21

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

Reconsideration and withdrawal of the obviousness rejection of

claims 34, 16, 18 and 19 over German '551 are earnestly requested.

2.   Fiber/Delivery Device/Pharmaceutical
      Composition Claims 24-33

A feature of claims 24-33 is a biodegradable silica fiber

having a solubility in simulated body fluid of from 0.2 to 20 wt-

%/h.

German '551 fails to raise a prima facie case of obviousness

against the claimed fiber (and delivery device, pharmaceutical

composition and method of treatment based thereon) because this

reference fails to disclose or suggest the solubility range

required by the claimed fiber (which will result in complete fiber

dissolution in about 21 days for the lower (slower) dissolution

range limit).   In contrast, German '551 discloses a fiber whose

fastest dissolution time is 50 days.

The Official Action appears to argue that "different criteria"

resulted in different dissolution parameters for the German '551

fibers. However, there is no support for this assertion. Instead,

German '551 states the biodegradability of its fibers should be

adjusted for both fast healing tissue and slowly occurring healing

processes (Translation, page 3, lines 15-18).

22

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

One of ordinary skill in the art would consider this
difference in fiber dissolution times (21 days *vs.* 50 days) to be
unexpected or surprising. Silica fibers with such fast dissolution
times simply had not been achieved by the prior art, as
demonstrated by both German '551 (dissolution times of 50 days or
more) and Ahola et al. (dissolution time of 40 weeks). One or
ordinary skill in the art simply would not have believed silica
fibers with such a fast dissolution rate (0.2 to 20 wt-%/h) could
be prepared.

Reconsideration and withdrawal of the obviousness rejection of
claims 24-33 over German '551 are earnestly requested.

It is believed this application is in condition for allowance.
Reconsideration and withdrawal of all rejections of claims 16, 18,
19 and 24-34, and issuance of a Notice of Allowance directed to
those claims, are earnestly requested. The Examiner is urged to
telephone the undersigned should she believe any further action is
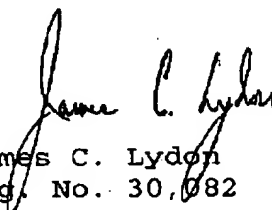required for allowance.

A Petition and fee for an Extension of Time are attached. It
is not believed any additional fee is required for entry and
consideration of this Amendment. Nevertheless, the Commissioner is

23

U.S. Appln. S.N. 09/913,643   **PATENT**
AMENDMENT

authorized to charge our Deposit Account No. 50-1258 in the amount

of any such required fee.

                          Respectfully submitted,

                          James C. Lydon
                          Reg. No. 30,082

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Enclosures:
     Petition for Extension of Time
     Sakka et al., "The Sol-Gel Transition in the Hydrolysis of
Metal Alkoxides in Relation to the Formation of Glass Fibers and
Films," 48 J. Non-Crystalline Solids 31-46 (1982).

24

31

THE SOL–GEL TRANSITION IN THE HYDROLYSIS OF METAL ALKOXIDES IN RELATION TO THE FORMATION OF GLASS FIBERS AND FILMS

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The sol–gel transition of $Si(OC_2H_5)_4$ was investigated by measuring the volume, the density, the SiO_2 content, the viscosity and the specific and intrinsic viscosities of the solution. The transition behavior of $Si(OC_2H_5)_4$ solutions with different amounts of water and different catalysts was compared. The measurements indicated that solutions with a small water content were comprised of linear polymer when catalyzed by HCl. Fibers could be easily drawn from such solutions immediately before gelation. Solutions catalyzed by HCl and containing a large amount of water behaved similarly to solutions catalyzed by NH_4OH, suggesting that a high water content causes the formation of non-linear or network colloidal polymers in hydrolysis–polycondensation. Such solutions did not exhibit spinnability but gelled into elastic bulk masses which were easily converted to bulk glasses.

1. Introduction

The alkoxide method for preparing oxide glasses in which the gels obtained as a result of the hydrolysis and accompanying polycondensation of metal alkoxides are converted to the corresponding oxide glasses by heating at relatively low temperatures has been developed as a new technique [1–3]. This method provides oxide glasses which are difficult to prepare by the conventional melting technique. SiO_2 glass and many other multicomponent oxide glasses [3–5] have been produced by the alkoxide method as fibers, thin films, coating films and monolithic bodies.

The transitions of gels to oxide glasses have been studied by many investigators [3,6] by thermal analysis, X-ray diffraction, infrared spectroscopy, picnometric measurement, electron microscopy etc. However, only a few works have been reported on the sol–gel transition of metal alkoxides. The objective of the present study is to investigate the sol–gel transition occurring in the hydrolysis and polycondensation of silicon tetraethoxide $Si(OC_2H_5)_4$ by measuring the density, the viscosity, the intrinsic viscosity etc., of the solution. The transition behavior is compared between the different alkoxide solutions for SiO_2 glasses; some of them are suitable for the preparation of fibers and others for bulk bodies. The type of polymeric product which might influence the spinnability and the ability to solidify without heavy cracking is also discussed.

32   S. Sakka, K. Kamiya / The hydrolysis of metal alkoxides

Table 1
Compositions of the $Si(OC_2H_5)_4$ solutions used in the study

Solution	$Si(OC_2H_5)_4$ (g)	H_2O (g)	C_2H_5OH (g)	Mole ratio of H_2O to $Si(OC_2H_5)_4$	Volume (cc)	SiO_2 content (g/100 cc)	Catalyst*
I	169.5	14.7	239.7	1	510	9.61	HCl
II	382.0	33.0	83.4	1	550	20.1	HCl
III	169.5	292.8	37.5	20	500	9.80	HCl
IV	50	3.8	47.6	1	118	12.2	NH₄OH
V	50	7.6	47.6	2	120	12.0	NH₄OH

* Mole ratio of HCl or NH₄OH to the $Si(OC_2H_5)_4$ is 0.01.

2. Experimental

2.1. Preparation of alkoxide solutions

Silicon tetraethoxide $Si(OC_2H_5)_4$ supplied by Wako Chemicals Co. was used as a starting material. Calculation shows that the SiO_2 content of this chemical corresponds to 28.9 wt%. Five alkoxide–water–ethanol mixture solutions were prepared, the compositions of which are listed in table 1. Water was required for the hydrolysis. Ethanol was used for diluting the alkoxide. Hydrogen chloride HCl and ammonium hydroxide NH_4OH were used as catalysts for hydrolysis.

The water contents were adjusted so that the mole ratios of water to alkoxide were unity for solutions I, II and IV, twenty for solution III and two for solution V, respectively. The mole ratio of water to alkoxide equaling unity corresponds to half the amount of water required for the complete polycondensation of $Si(OC_2H_5)_4$ into SiO_2, assuming eq. (1) for hydrolysis, eq. (2) for polycondensation and eq. (3) for the net reaction.

$$nSi(OC_2H_5)_4 + 4nH_2O \rightarrow nSi(OH)_4 + 4nC_2H_5OH, \tag{1}$$

$$nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O, \tag{2}$$

$$nSi(OC_2H_5)_4 + 2H_2O \rightarrow nSiO_2 + 4nC_2H_5OH. \tag{3}$$
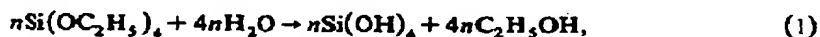
The amount of ethanol was adjusted so that the concentration of the alkoxide which is expressed as the SiO_2 content in grams per 100 cm^3 of the solution is alike for solutions I, III, IV and V. The concentration of alkoxide in solution II is about two times larger than that in the others. The hydrogen chloride HCl was used as a catalyst for solutions I, II and III, and NH_4OH for solutions IV and V. The mole ratio of catalyst to alkoxide was kept at 0.01 for all the solutions.

In order to prepare clear solutions without any precipitation, the alkoxide was diluted with half the amount of ethanol listed in table 1, and then the mixed solution consisting of the specified amount of water and another half of the ethanol containing HCl or NH_4OH was added drop by drop to the alkoxide–ethanol mixture solution from a burette under continued stirring. These operations were carried out at room temperature. The addition of the water–ethanol mixture to the alkoxide had to be made slowly, otherwise white fluocculent precipitates resulted, especially when NH_4OH was used as a catalyst for hydrolysis. The solutions thus prepared were kept standing at 25°C in the ambient atmosphere without any cover.

2.2. Measurements of volume, density and SiO_2 content of the solutions

The volume and weight of the alkoxide solution were measured at certain intervals while it was kept at 25°C until its gelling. The density of the solution was determined by weighing 10 cm^3 of the solution at 25°C. In order to

determine the SiO_2 content, 100 cm^3 of the solution was forcibly hydrolyzed and condensed to SiO_2 gel by adding concentrated ammonia water. The resulting gel was heated at 500°C or higher temperatures to remove volatile matter such as water and ethanol and then weighed.

2.3. Measurement of viscosity of the solution

The viscosity of alkoxide solutions was measured at 25°C. An Ostwald type viscometer was used for the viscosity range of a few centipoise to about 0.5 P. The viscosity above about 0.5 P was measured with the balanced sphere technique. Two polysiloxane polymers (silicone oil) TSF 451-1 M and TSF 451-10 M supplied by Toshiba Silicone Company and with known viscosities were used as references.

2.4. Determination of intrinsic viscosity

It is known that the reduced viscosity η_{sp}/C of a polymer solution can be expressed by the following Huggins' equation [7], if polymers dissolved in the solution are chain-like or linear.

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C, \tag{4}$$

where

$$\eta_{sp} = \eta_{rel} - 1. \tag{5}$$

Here, η_{sp}, η_{rel}, $[\eta]$, k and C are the specific viscosity, the relative viscosity, the intrinsic viscosity, a proportionality constant and the concentration of the polymer, defined usually as grams in 100 cm^3 solution, respectively. The intrinsic viscosity $[\eta]$ is defined as the reduced viscosity of the polymer at its infinite dilution and can be determined by extrapolation of the η_{sp}/C versus C relation to zero concentration of the polymer.

On the other hand, the reduced viscosity η_{sp}/C of the solution containing spherical particles is expressed by the following equation [8].

$$\eta_{sp}/C = K/\rho = 0.025/\rho, \tag{6}$$

where K is a constant, ρ is the density of colloidal particles and C is the concentration of the polymer. This equation indicates that η_{sp}/C is independent from the concentration and particle size if the polymers are spherical.

Therefore, it will be possible to predict the shape of polymers produced in the alkoxide solution from the variation of the reduced viscosity as a function of the concentration of the solution. In this work, the reduced and intrinsic viscosities were measured at 25°C using an Ostwald type viscometer for solutions I, III and V of which the initial SiO_2 concentrations are similar. The concentrations of the starting solution taken at various stages of the reaction for the η_{sp}/C measurement were determined as described in the above section. Anhydrous ethanol (99.5% pure) was used for diluting the starting solution.

3. Results

3.1. Appearance and spinnability of alkoxide solutions

Solutions I, II and III containing HCl as catalyst for hydrolysis remained clear during hydrolysis and polycondensation. Transparent gelled masses resulted. On the other hand, solutions IV and V catalyzed by NH_4OH were clear just after preparation but became faintly cloudy, and the resultant gels were less clear than the above three gels. The cloudy appearance of these solutions may indicate that colloidal particles are involved in the solutions.

Times required for gelling and occurrence of spinnability of the solutions are given in table 2. The gelling point of the solution was defined as the time at which the solution loses fluidity, namely no flow of the solution is observed on tilting the container.

Solutions I and II with small amounts of water relative to the content of $Si(OC_2H_5)_4$ exhibited remarkable spinnability just before gelling as already reported. Fibrous gels were easily produced from those solutions by immersing a glass rod in the solution and pulling it up. Solution III with a large amount of water and catalyzed by HCl and solutions IV and V catalyzed by NH_4OH showed no spinnability before gelling. Those solutions were solidified into bulk elastic gels.

Examination of spinnability was made on many solutions other than those listed in table 1. Solutions of varying water contents in which the mole ratio of water to alkoxide ranged from 1 to 4 and NH_4OH of mole ratios ranging from 0.001 to 0.1 were examined. No spinnability was exhibited by the alkoxide solution as long as NH_4OH was used as the catalyst for hydrolysis.

3.2. Variation of volume, density and SiO_2 concentration of the solutions with time

The volume, the density and the SiO_2 concentration of the solutions are shown in figs. 1, 2 and 3, respectively, as functions of the relative standing times t/t_g, where t_g is the time required for gelling.

It can be seen from fig. 1 that the decrease in the volume of solutions I and

Table 2
Times required for gelling and occurrence of spinnability of the $Si(OC_2H_5)_4$ solution at 25°C

Solution	Time for gelling (h)	Spinnability	Appearance of the solution and gel
I	525	yes	transparent
II	360	yes	transparent
III	248	no	transparent
IV	565	no	slightly flocculent
V	742	no	slightly flocculent

36   S. Sakka, K. Kamiya / The hydrolysis of metal alkoxides

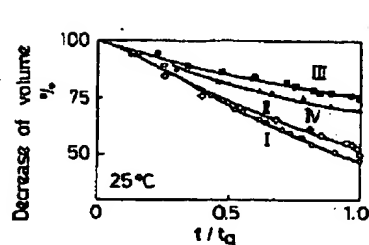

Fig. 1. Variation of the volume of $Si(OC_2H_5)_4$ solutions with the relative time t/t_g. O, solution I; ◇, solution II; ■, solution III; ▲, solution IV.
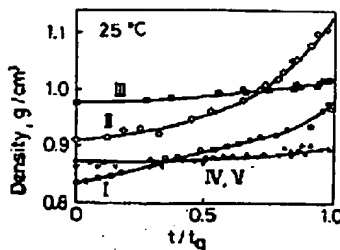
Fig. 2. Variation of the density of $Si(OC_2H_5)_4$ solutions with t/t_g. O, solution I; ◇, solution II; ■, solution III; ▲, solution IV; ▼, solution V.

II with time is more rapid than that of solution III. It can also be seen that the change in the volume of solution III is similar to that for solution IV. This indicates that the solution with a large amount of water behaves similarly in volume change to the solution catalyzed by NH_4OH.

The density of the starting solution depends on the composition of the solution. It can be seen, however, that the rate of increase in the densities of solutions I and II is larger than those of other solutions. It should be noticed that solution III, which contains a large amount of water, displays a similar density change to that of solution IV, which is catalyzed by NH_4OH. The SiO_2 content obtained from the alkoxide solutions was found to be unchanged until gelling was attained. This indicates that evaporation of the starting alkoxide $Si(OC_2H_5)_4$ does not occur through the reaction. The decrease of the volume of the solution, therefore, can be ascribed to evaporation of volatile matter such as excess water, ethanol added beforehand and ethanol produced through
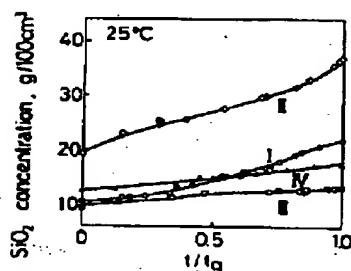

Fig. 3. Variation of the SiO_2 concentration of $Si(OC_2H_5)_4$ solutions with t/t_g. O, ●, solution I; ◇, ◆, solution II; ■, □, solution III; △, solution IV. Open symbols denote calculated values and full symbols observed values.

the hydrolysis and polycondensation of $Si(OC_2H_5)_4$. The densities above unity attained in solutions II and III (fig. 2) can be explained by the formation of polymers of density larger than unity, since the densities of $Si(OC_2H_5)_4$, ethanol and water are smaller than unity at 25°C. The densities of solutions I, IV and V are smaller than those of solutions II and III due to dilution. However, it is assumed that the formation of polymers may contribute to the increase of the densities of these solutions, together with the decrease of the volume due to evaporation of volatile matters.

The SiO_2 concentrations calculated from the volume and weight of SiO_2 initially contained in the solution are shown in fig. 3. The SiO_2 concentrations determined experimentally by hydrolyzing 100 cm^3 of the solution forcibly with concentrated ammonia water and heating the resulting gels at 500°C are represented in the same figure by full symbols. The calculated values agree well with the experimentally determined ones. The changes of the SiO_2 concentrations of solutions I and II with time are similar and more abrupt than that of solution III. This solution, with a large amount of water, shows a similar concentration change to solution IV which contains NH_4OH as catalyst.

3.3. Variation of viscosity of the solutions with time

The viscosities of the five $Si(OC_2H_5)_4$ solutions are shown as functions of time in fig. 4. The viscosity at which the solution gels is also shown in this figure by crosses. The difference in viscosity between the initial solutions (at $t = 0$) can be attributed to the difference in composition between the solutions.

It can be seen that solution III becomes viscous and gels in a shorter time than other solutions. This indicates that a larger water content promotes the hydrolysis and polycondensation reaction. It can also be seen that solution II becomes viscous and gels in a shorter time than solution I, indicating that the higher SiO_2 concentration causes a faster reaction when the mole ratio of water added to the alkoxide is the same. It can also be seen that solutions I and II which contain HCl as catalyst undergo gelation in shorter times than solutions IV and V which contain NH_4OH.

It should be remarked that the viscosity of the solution at which gelation occurs is about 10 times lower for solutions III, IV and V than that for solutions I and II. Namely, the viscous state lasts for relatively long time in solutions I and II, but solutions III, IV and V lose fluidity at lower viscosities. This behavior is assumed to be related to the occurrence or non-occurrence of the spinnability of the solution. It should be recalled that solutions I and II show remarkable spinnability.

The viscosities of the solutions are plotted against the relative time t/t_g in fig. 5. In this figure, the initial viscosity of the solution ($\eta_{t=0}$) is normalized to that of solution I. It can be seen that solutions I and II, which exhibit remarkable spinnability, display a different type of viscosity change from solutions III, IV and V which exhibit no spinnability. A small water content combined with the HCl catalyst causes a gradual increase of the viscosity
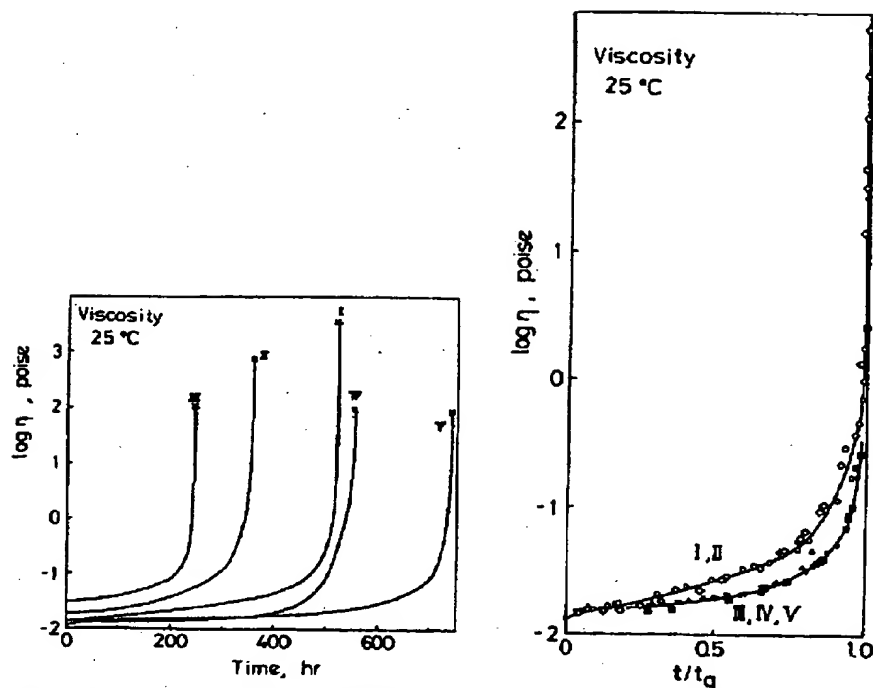
Fig. 4. Variation of the viscosity of Si(OC₂H₅) solutions with time. Crosses indicate the viscosity at which the solution gels.

Fig. 5. Variation of the viscosity of Si(OC₂H₅)₄ solutions with t/t_g. Initial viscosity of solutions is normalized to that of solution I. O, solution I; ◇, solution II; ■, solution III; ▲, solution IV; ▼, solution V.

(solutions I and II), while a large water content and NH₄OH catalyst causes a more abrupt increase of the viscosity.

3.4. Reduced and intrinsic viscosities

Fig. 6 shows the reduced viscosity η_{sp}/C of solutions taken during hydrolysis for solution I plotted against the concentration expressed as the SiO₂ content in a 100 cm³ solution. The results for a Ludox solution (Du Pont, HS-40) which contains about 40 wt% of spherical colloidal SiO₂ particles and a sodium metasilicate solution which consists of chain-like polysiloxane polymers are also shown in fig. 6 for comparison. The behavior of two kinds of silicone oil is shown in fig. 7. The Ludox solution shows almost no dependence
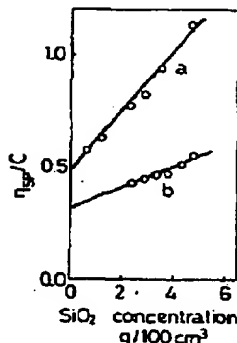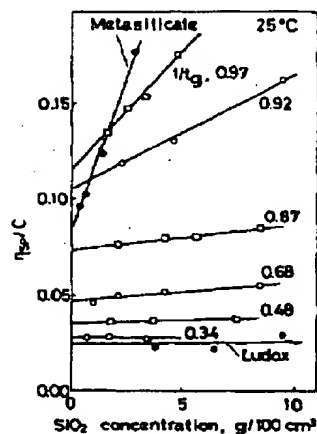
Fig. 6. Concentration dependence of the reduced viscosity η_{sp}/C of solution I at varying t/t_g during hydrolysis at 25°C. The attached numbers denote t/t_g.

Fig. 7. Concentration dependence of the reduced viscosity η_{sp}/C of two silicone solutions. a, TSF 451-10 M; b, 451-1 M (Toshiba Silicone Company).

of η_{sp}/C on C and the small intrinsic viscosity $[\eta]$ as suggested by eq. (6), while the metasilicate and silicone solutions show a large concentration dependence of η_{sp}/C on C according to eq. (4).

For solution I, the concentration dependence of η_{sp}/C cannot be seen at the early stage of the reaction (curve for $t/t_g = 0.34$) and the corresponding value of $[\eta]$ is small. The linear dependence of η_{sp}/C becomes appreciable and the corresponding value of $[\eta]$ becomes larger for $t/t_g = 0.48$. Then, the concentration dependence of η_{sp}/C and $[\eta]$ becomes much larger as the hydrolysis and polycondensation reaction progresses. This indicates that chain-like or linear polymers are produced through hydrolysis of solution I as in the metasilicate and silicone solutions.

Fig. 8 shows the plot of η_{sp}/C against C for solution V which is catalyzed by NH$_4$OH. The concentration dependence of η_{sp}/C cannot be seen even at $t/t_g = 0.75$, whereas a linear dependence can be seen at $t/t_g = 0.998$.

Variation of the intrinsic viscosity $[\eta]$ with the relative time t/t_g is shown for solutions I, III and V in fig. 9. It can be seen that $[\eta]$ of solution I increases gradually with increasing time, while $[\eta]$ of solutions III and V remains almost constant at small values of t/t_g up to about 0.6 and then increases abruptly as the gelling point is approached.
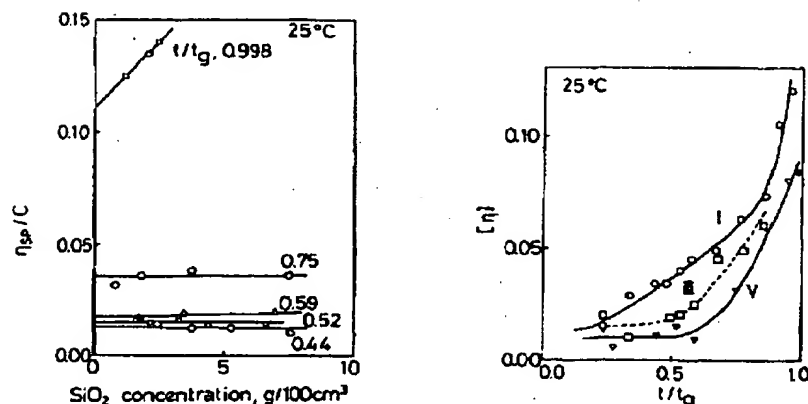
Fig. 8. Concentration dependence of the reduced viscosity η_{sp}/C of solution V at varying t/t_g during hydrolysis at 25°C.

Fig. 9. Variation of the intrinsic viscosity $[\eta]$ of $Si(OC_2H_5)_4$ solutions with t/t_g at 25°C. O, solution I; □, solution III; ▽, solution V.

4. Discussion

The effect of the amount of water and the kind of catalyst on the variation of the properties of $Si(OC_2H_5)_4$ solutions with time has been investigated. It has been found that the solutions can be divided into two groups on the basis of the trend of property variation. Alkoxide solutions with a small water content and HCl catalyst constitute one group, and solutions with a large water content and solutions catalyzed by NH_4OH constitute another group. It should be remembered that the former can be drawn into fibers but the latter cannot.

4.1. Hydrolysis of $Si(OC_2H_5)_4$ solution catalyzed by NH_4OH

It has been known for some time that spherical colloidal particles are formed when the hydrolysis–polycondensation of $Si(OC_2H_5)_4$ is carried out with NH_4OH as catalyst. Nogami and Moriya [9] observed spherical SiO_2 particles of about 100 Å in diameter under an electron microscope in the gel produced from $Si(OC_2H_5)_4$ catalyzed by NH_4OH. Yamane [10] has shown on the basis of small angle X-ray scattering that colloidal particles are formed in an early stage of hydrolysis of $Si(OCH_3)_4$ with ammonia water. They are aggregated to form larger particles as the reaction progresses. Monodispersed colloidal SiO_2 spherulites [11] have been produced from $Si(OC_2H_5)_4$ solution by hydrolysis with NH_4OH.
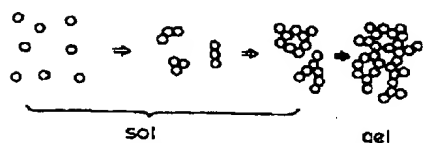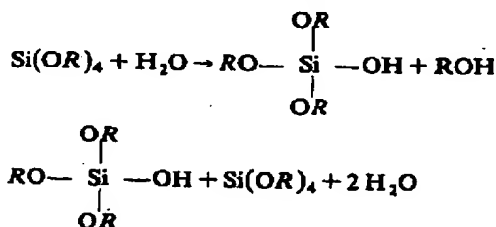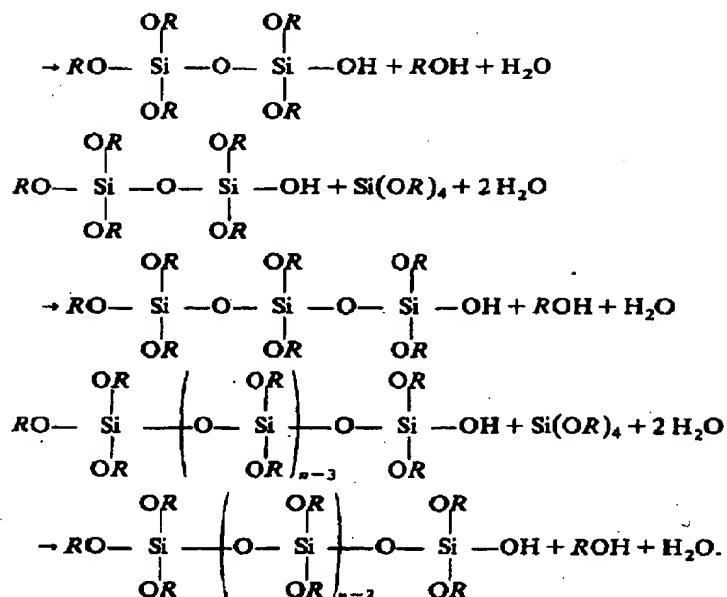
Fig. 10. Schematic representation of the aggregation of colloidal SiO_2 particles to form the network structure in NH_4OH catalyzed $Si(OC_2H_5)_4$ solutions.

In the present study, slightly cloudy precipitates have been produced in the alkoxide solution catalyzed with NH_4OH as the reaction has progressed. The fact that almost no concentration dependence is found for the reduced viscosity η_{sp}/C and that the intrinsic viscosity $[\eta]$ is small up to the relative time t/t_g of about 0.6 can be interpreted as showing that spherical colloidal SiO_2 particles are formed in the solutions catalyzed by NH_4OH. The abrupt increase of the viscosity η and the intrinsic viscosity $[\eta]$ near the gelling point may be ascribed to aggregation of discrete spherical SiO_2 particles which may finally lead to a three-dimensional network structure. The formation of aggregates is schematically shown in fig. 10. Such aggregates have been observed in a gel by Nogami and Moriya [9]. Because those aggregates have an open structure (which can be understood from the small SiO_2 concentration in solutions IV and V catalyzed by NH_4OH), they might be easily deformed to rod-like shapes when the solution is passed through a capillary tube. This might result in the large concentration dependence of η_{sp}/C and a large $[\eta]$ value immediately before gelling

4.2. Hydrolysis of $Si(OC_2H_5)_4$ solution catalyzed by HCl

Two moles of water are required for complete hydrolysis–polycondensation of one mole of $Si(OC_2H_5)_4$ into SiO_2 of threedimensional network structure as shown in eqs. (1)–(3). Boyd [12] and Bradley [13] reported that chain-like polymers are formed as a result of the hydrolysis–polycondensation of titanium alkoxide when the amount of water is small. If it is assumed that $Si(OC_2H_5)_4$ is similar to titanium alkoxide in hydrolysis–polycondensation behavior, the following formulae will be valid when the water content is small.

$$Si(OR)_4 + H_2O \rightarrow RO-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{Si}}-OH + ROH$$

$$RO-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{Si}}-OH + Si(OR)_4 + 2H_2O$$

$$\rightarrow RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH + ROH + H_2O$$

$$RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH + Si(OR)_4 + 2\,H_2O$$

$$\rightarrow RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH + ROH + H_2O$$

$$RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!\left(\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!\right)_{\!\!n-3}\!\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH + Si(OR)_4 + 2\,H_2O$$

$$\rightarrow RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!\left(\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!\right)_{\!\!n-2}\!\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH + ROH + H_2O.$$

The net hydrolysis–polycondensation reaction is shown by the following formula.

$$nSi(OR)_4 + nH_2O \rightarrow RO\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!\left(\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!\right)_{\!\!n-2}\!\!-\!O\!-\!\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{Si}}\!-\!OH$$

$$+ (2n - 1)ROH. \tag{7}$$
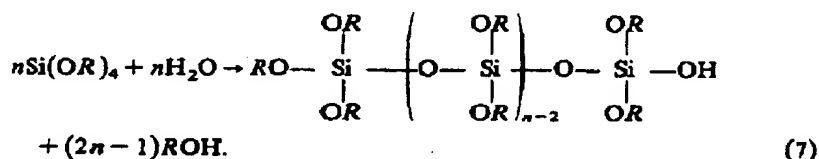
This indicates that the addition of one mole of water to one mole of $Si(OC_2H_5)_4$ is required to produce chain-like polysiloxane polymers.

Actually, the variation of the properties of alkoxide solutions I and II characterized by a small water content combined with HCl catalyst is different from that of solutions IV and V which contain spherical colloidal SiO_2. Occurrence of the concentration dependence of η_{sp}/C for solution I in an early stage hydrolysis–polycondensation suggests that polymeric products in the solution are not spherical but linear. The increase of the intrinsic viscosity $[\eta]$ with time implies that the degree of polymerization increases with time. In general, solutions containing linear polymers are more viscous than those containing spherical polymers if comparison is made at the same polymer concentration. The higher viscosities of solution I than solutions IV and V which are catalyzed by NH_4OH may also be evidence for the presence of linear polymers in the former solution.

The behavior of solution III was more similar to solutions IV and V which contain spherical polymers than to solutions I and II which contain linear polymers. The small concentration dependence of η_{sp}/C and small $[\eta]$ values below t/t_s of about 0.7 for solution III suggest that non-linear or spherical polymers are produced in solution III as in solutions IV and V. The rapid increase of $[\eta]$ of solution III in the final stage of the reaction may be attributed to aggregation of non-linear polymers to larger network polymers. At present, it is difficult to give an exact explanation to the type of polymers produced in solution III. More information such as the molecular weight of the polymers is required to approach this problem.

4.3. Occurrence and significance of spinnability

Hirai [14] examined the occurrence of spinnability in many kinds of polymer solutions and came to the conclusion that only the solutions containing linear polymers were spinnable. On this basis, the present authors assumed the formation of linear polymers in the alkoxide solutions exhibiting remarkable spinnability [3]. This assumption has been proved to be true in the present study. Namely, it has been found that linear polymers are produced from the $Si(OC_2H_5)_4$ solution through hydrolysis–polycondensation when the amount of water is small and HCl is used as catalyst. Fibers could be drawn from such solutions.

Once fibrous gels are obtained from $Si(OC_2H_5)_4$ solution, they are easily converted to SiO_2 glass fibers by heating to 600–1000°C. No breakage is seen when the fibrous gels are put into the furnace at high temperature.

It can be seen in table 2 that as much as 300–500 h is required for us to obtain a spinnable solution when the solution is kept at 25°C. It has been found, however, that the temperature at which the solution is kept standing does not affect occurrence of spinnability. Thus, heating of the $Si(OC_2H_5)_4$ solution at 80°C has enabled us to draw fibers in 2 to 3 h after preparation of the solution. Fig. 11 shows an example of variation of viscosity for an $Si(OC_2H_5)_4$ solution kept at 80°C. The viscosities were measured at 25°C. It can be seen that the viscosity reaches about 10 P in about 3 h at which time fibers can be drawn from the solution.

In the present study, the use of HCl as a catalyst has been found to give a spinnable solution when the water content of the solution is small. The use of acetic acid is also known to produce spinnability in the solutions [15]. Table 3 shows occurrence of spinnability in alkoxide solutions for 10 TiO_2. 90 SiO_2 in wt% in which CH_3COOH is used as a catalyst [15]. It is concluded that an acid catalyst will provide us with a spinnable solution as long as the water content is small.

Occurrence of spinnability can be applied to the preparation of thin glass films. Gel films are made by drawing from a viscous alkoxide solution through a slit or by scooping a film from the viscous solution using a wire ring. This can be achieved when an alkoxide solution with a small water content is used

Table 3
Occurrence of spinnability in solutions for 10 TiO_2 90 SiO_2 (wt%) glasses [15]

Solution [a]		Temp. (°C)	Gelling time (days)	Spinnability	Shape of gel
H_2O	CH_3COOH				
(mole ratio) [b]					
1	0.003	30	5	yes	powder
2	0.03	30	7	yes	powder
4	0.3	30	6	yes	powder
8	0.3	30	7	no	powder
10	0.03	15	24	no	piece
25	0.00043	26	24	no	piece
25	0.38	26	23	no	piece

[a] Composition: $Ti(O isoC_3H_7)_4$ 2 g, $Si(OC_2H_5)_4$ 17.54 g, C_2H_5OH 40 ml. Amounts of H_2O and CH_3COOH are varied.
[b] (H_2O)/(alkoxides) and (CH_3COOH)/(alkoxides).

which displays spinnability as in fiber drawing. The gel film thus prepared can be converted to SiO_2 glass films by heating at 600–900°C.

There is another technique by which to obtain a spinnable alkoxide solution. In this technique water is not added to the initial alkoxide solution. Instead, the solution is kept open to atmosphere so that it can absorb moisture from the air. This technique has been employed to make TiO_2–SiO_2 [16] and ZrO_2–SiO_2 [17] glass fibers. It has been observed that the viscosity of the solution slowly increases with time until spinnability appears before gelling. It is believed that carbon dioxide gas is absorbed together with water and acts as a catalyst for hydrolysis. It is assumed that this corresponds to the case of small water content in the present experiments, considering that absorption of water from the air progresses very slowly.
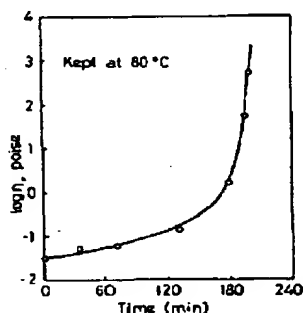

Fig. 11. Variation of the viscosity with time for an $Si(OC_2H_5)_4$ solution at 80°C. Viscosities measured at 25°C. The composition of the solution: $Si(OC_2H_5)_4$ 165.8 g, C_2H_5OH 45 ml, 2.06 N HCl 3.9 ml, H_2O 2.5 ml. The ratio (H_2O)/$[Si(OC_2H_5)_4]$ is 2.04.

S. Sakka, K. Kamiya / The hydrolysis of metal alkoxides   45

4.4. Significance of large water content

It has been found that a large water content favors the formation of non-linear or network polymers in the hydrolysis of $Si(OC_2H_5)_4$. The increase in viscosity of the solution containing network polymers in the final stage of the reaction is probably due to aggregation of those polymers. It is supposed that this gives the solution an elastic nature, which prohibits the occurrence of spinnability. Accordingly the solution becomes an elastic gel without showing any spinnability.

On the other hand, it has been shown that the addition of a large amount of water to a metal alkoxide favors the manufacture of monolithic bulk gels and bulk oxide glasses [3]. The reason for this is not yet clear. It can be stated, however, that there are many other important factors to be considered, such as the porosity of the gel and the heating rate, in order to obtain bulk oxide glasses.

5. Summary

Various properties of $Si(OC_2H_5)_4$ solutions have been measured as functions of time during hydrolysis and the accompanying polycondensation. The effects of varying water content and kind of catalyst on property variations of the alkoxide solutions have been examined and related to the occurrence of spinnability. The results are summarized as follows.

(1) Alkoxide solutions containing a small amount of water combined with an HCl catalyst become spinnable before gelling, while solutions with a large water content and solutions catalyzed by NH_4OH undergo gelling without exhibiting spinnability. On this basis the solutions can be classified into group I (the former) and group II (the latter).

(2) The variation of the volume, the density and the SiO_2 content of solutions belonging to group I is different from those belonging to group II.

(3) The reduced viscosity η_{sp}/C of a solution (group I) containing a small amount of water combined with an HCl catalyst shows concentration dependence throughout the process of hydrolysis–polycondensation, which is characterized by the presence of linear polymers. This is interpreted to be the reason for the occurrence of spinnability.

(4) The reduced viscosity η_{sp}/C of a solution catalyzed by NH_4OH (group II) has no concentration dependence except immediately before gelling. This is attributed to the presence of spherical particles in the solution and is assumed to be the reason for non-spinnability.

(5) Both gel fibers and films can be drawn from the spinnable solutions with small amounts of water and converted to SiO_2 glasses by heating at 600–900°C.

46   *S. Sakka, K. Kamiya / The hydrolysis of metal alkoxides*

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